

THE EISENHOWER LIBRARY

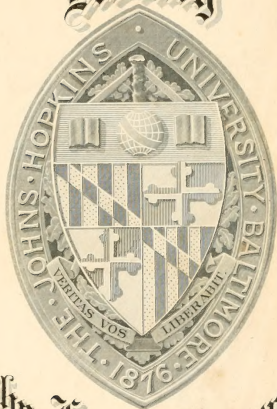


3 1151 02564 2327

MORAVIA
SPEC. COLL.

54.441

Library



Johns Hopkins
of the
University

JAV THESIS
Parks,
R. M.
1892
C. 1

On The Action
of Methyl Alcohol
on
Para-Di-azo-Ortho-Toluene
Sulphonic Acid.

Dissertation
Presented for the Degree
of
Doctor of Philosophy
at the
Johns Hopkins University

by
R. M. S. Sarks, Jr.
1892

Contents

Introduction	1.
Preparation of para-toluidine orthosulphonic acid.	7.
Preparation of Meitzner compound	12.
Decomposition of Meitzner	14.
Decompositional ordinary pressure	17.
Decompositional increased pressure	26.
Decompositional diminished pressure	27.
Para-methoxy-ortho-toluenesulphonic acid	33.
Barium salt of same	35.
Calcium salt of same	36.
Magnesium salt of same	37.
Zinc salt of same	39.
Sodium salt of same	40.
Potassium salt of same	41.

Para-methoxy ortho-toluenesul- phonic chloride	42.
Para-methoxy ortho-toluenesul- phonic anhydride	44.
Comparison of the methoxy tol- uenesulphonic acid with the oxy-methyl sulphonic acid of Thompsett and Keffler	47.
Para-methoxy benzyl sulphinate	48.
Potassium salt of same	45.
Para-methoxy ortho-methyl benzyl acid, $\frac{1}{2}$	
Acid potassium salt of same	67.
Acid potassium salt of same	70.
Chloride of methoxy isophthalic acid	74.
Comparison of Para-methoxy ortho- sulphobenzyl acid with sulfo- cinic acid.	75.
Preparation of humic acid	75.
Protocatechuic acid	77.



Analysis of milk of *Capri* (cattle)
milk with potassium hydroxide 71.
Beta-resorcylic acid 70.
Secondary 73.

Acknowledgement.

The work described in this paper
was carried on in the chemical lab-
oratory of Johns Hopkins University at
the suggestion and under the im-
mediate supervision of Professor
Sawyer. It is a pleasure to record here
an expression of gratitude for the
instruction and advice received
from him during my course at
this university. I owe much also
to the instruction received from
Professor Morse in quantitative anal-
ysis and Professor Williams
in mineralogy and geology.

Introduction.

The investigation, of which an account is given here, was undertaken for the purpose of studying the decomposition of para-diazotoluene sulphonic acid in methyl alcohol. A description of some transformations of the product of the reaction follows.

The decomposition of diazo compounds in different alcohols has been studied, as is known, in a large number of cases, since the first discovery of these compounds by Griess in 1860. The results first reached by Griess led him to make the general statement that diazo compounds are decomposed by boiling alcohol the same way

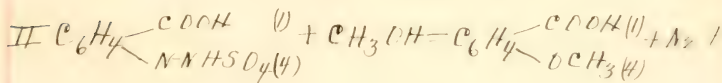
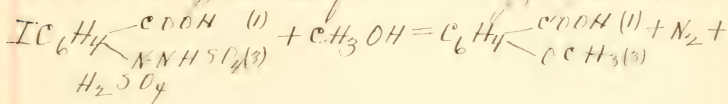
is eliminated and hydrogen takes
its place, this so called Fries
or hydrogen reaction suggested
an convenient method for the replace-
ment of the amide, respectively the
nitro group by hydrogen.

This method however was not
found to be applicable in all cases.
Many experimenters, notably among
the first Wroblewsky, in attempting
the replacement of the nitro or amide
group with hydrogen, by converting
into the diazo compound and decom-
posing with ordinary electrical cur-
rent found that ethoxy compounds re-
sulted instead of hydrogen. The
conditions which are favorable to
the hydrogen or ethoxy reactions
have been studied in a number

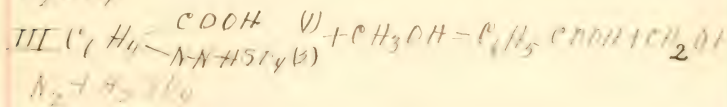
of cases. These investigations have led to interesting suggestions as to the influence of the position and presence of certain groups in the benzene nucleus, also the influence of the solution of the alcohol and pressure on the course of the reaction. The alcohol used generally in these experiments has been ethyl alcohol. Differences were found when some imide or compound was decomposed by different alcohols, as methyl, ethyl and isopropyl alcohols. The data in regard to the course of the reaction when methyl alcohol is used were not very numerous.

Kofmann had observed that camidide or amido-tri-methyl benzene was

dissolved and decomposed with
 methyl, ethyl, and amyl alcohols gave
 the corresponding ethers of tri-methyl
 phenol. He also obtained anisol
 $C_6H_5OCH_3$ from diazo benzene and
 methyl alcohol. Griss mentions the
 conduct of the tri-diazo benzene
 acids with methyl alcohol. "The
 meta and para gave only methoxy
 products," the ortho gave benzic acid
 according to the following equations.



H_2SO_4



(Beckmann) 971

Graham of this laboratory in the same year 1888 had observed the formation of anisic acid according to equation II.

Two decompositions of diazo compounds with methyl alcohol with variation of pressure have been made, both in this laboratory. Metcalf¹ studied the decomposition of para-diazo meta-sulfonic acid with methyl, ethyl and propyl alcohol. He draws two conclusions which have an important bearing on the course of the reaction. Increase of pressure and the simpler the alcohol, the greater the yield of alkyl product.

Richard² found that the yield of

¹/J. Soc. is 1890 ²/J. Soc. is 1892.

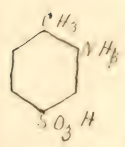
6
compound from substitution and
water melting alcohol gave only the
hydrogen product at less than
one half atmospheric pressure.
When heated together in a sealed
tube only the melting product was
formed.

The work of Mitaloff, mentioned above
and that of Hey, Luck, and Impricht
and Kieffler have the closest relation
to the investigation described in
this paper.

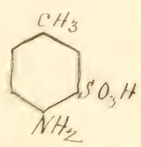
Hey, Luck in decomposing the liquid
compound of ortho-cresol para-
toluene sulphonic acid ^{with melting alcohol} at
ordinary pressure the melting pro-
duct mainly or the melting para-
sulphonic acid, or as Hey, Luck nam-
ed it, methyl cresol sulphonic acid

Gimbricht and Kieffer for one the diazo-compound derived from para-ortho-ortho-toluene sulfonic acid and methyl alcohol obtained para-methoxy-ortho-toluene sulfonic acid, "this acid is apparently identical with the acid obtained in this investigation and a comparison is described in the succeeding pages. The formulas of the amide-acid for one which the diazo-compounds were derived are given here. The last one is the one used in this investigation.

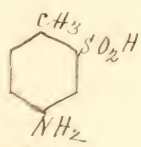
2



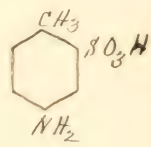
Hayduck



Metcalf



Kieffer



Preparation of pure toluene-
ortho-sulphonic acid.

The starting point of the present investigation was para-nitro-toluene. This compound together with fuming sulphuric acid was used by Kuhlberg and Bairstow for the purpose of preparing para-nitro-ortho-toluene-sulphonic acid. According to their directions one part of the nitro-toluene was treated with four parts of fuming sulphuric acid. The flask containing the mixture was lowered into water which was then heated to boiling temperature of water for four to five hours. After cooling the dark viscous liquid was poured into twelve plates of cold water.

1/11 molen 1.55-8



If any nitric solution had not been
 added up on by the sulphuric acid,
 this is filtered off, and after drying
 may be used again for the same ex-
 periment. The sulphuric acid to-
 gether with the excess of sulphuric
 acid was then neutralized by
 chalk, filtered through a cloth fil-
 ter from the gypsum, which should
 be repeatedly washed with hot wa-
 ter. The filtrate containing the
 calcium salt of the sulphuric
 acid was again filtered this time
 through paper, the calcium pre-
 cipitated by potassium carb-
 onate. The solution of the bismuth^{acet}
 was separated from the calcium
 carbonate by filtration and evap-
 orated to crystallization. The

Potassium salt thus obtained appeared as a mass of straw-colored crystals. This potassium salt was used for the reduction of the nitro group by zinc and HCl or by stannous acid, according to the method described by Brockitt and Neaves.

Five parts of the potassium salt, six parts of granulated zinc, thirty parts of commercial hydrochloric acid, were gently heated until the reaction began, where the heat was turned off. The reaction proceeded vigorously, constant stirring being kept up during the reduction, which was over in five minutes. After cooling the soluble salt of stannous chloride and the amino acid separated as a precipitate.

Am. Chem. Jour. 9, 379.

talline mass, this was collected in
 a funnel and freed from the
 mother liquor by suction, dissolved
 in water and treated with a
 solution of sodium carbonate to pre-
 cipitate the lime and make the sol-
 utable sodium salt of the malic acid.
 After filtering off the lime and the
 malic acid was precipitated from
 its sodium salt by hydrochloric acid.
 After dissolving in boiling water,
 treating with animal charcoal the
 acid was obtained in almost
 colorless rhomboidal crystals.
 The para-amale-ortho-bromosul-
 fonic acid is almost insoluble
 in cold water, difficultly so in
 hot water, insoluble in strong
 alcohol.

The reaction of the living compound
 of the various methods described
 in the literature for dissolving
 nitro compounds that if suspended
 in the individual compound
 in water was used for passing
 nitrous fumes through this mixture.
 Hargrave thus dissolved the isomeric
 compound ortho-toluidine-sulphonic
 acid.¹ The more specific
 directions given by Comstock and
 de Kock² proceed most advantageously.
 The part of finely divided re-
 sidual with suspended in coarse and
 one half part of water were shaken
 together cooled with ice water and
 a rapid current of nitrous fumes
 produced for conversion to nitro-
 acid (nitric acid (Sb. 22, 135)) is used

¹ Annalen 174-235 ² (Ann. Chem.)

passed through in about fifteen minutes the reaction is over. The diazo compound was then mixed with well cooled alcohol, filtered quickly with aid of the pump, and washed with ether. After removal from the filter the diazo compound was spread upon filtering paper. When the odor of ether is no longer perceptible the diazo ^{compound} is ready for further use. In this manner as much as 120 g of the amido acid were diazotized in fifteen minutes giving a yield of 90% by weight of the acid used. This diazo compound is colorless when first made but soon becomes bluish. At ordinary temperatures it is stable for months if kept in the dark brown

for absolute alcohol, mp condenses
at 130°C . Insoluble in alcohol and
ether, soluble in water which on
boiling gives free cresol-
sulfonic acid.

Decomposition of the dihydro-
compound with methyl alcohol.
It has already been stated in the
introduction that dihydro-
compounds in decomposing with alcohol, some-
times follow the hydrogenation reaction,
sometimes the alkene reaction or
both. "Dawson" had studied the
reaction of this same dihydro-
compound with ethyl alcohol under
various conditions of pressure
and had found that both the hy-
drogen and alkene compounds

were formed.

The isomeric compound viz, *para*-*di*-*ortho*-*meta*-toluenesulphonic acid has been studied by the *Leaf*, with methyl, ethyl, and *propyl* alcohols. Both the hydrogen and alkylation reactions resisted under pressure. *Hydrolysis* with *meta*-isomer, *ortho*-*di*-*ortho*-*para*-toluenesulphonic acid, obtained only the *ortho*-*propyl* product decomposing at ordinary pressure with methyl and ethyl alcohols. A preliminary experiment at ordinary pressure was made and it was found that the *di*-*ortho* compound decomposed with the methyl alcohol. On evaporating the methyl alcohol a dark heavy liquid having no acid reaction remained. This

acid was converted into the Berin
salt by treatment with pure barium
carbonate, and upon boiling the water
solution, there was deposited large
tabular crystals together with a
white powder. This result seemed
to indicate the formation of two
products, namely the hydrogen
and methoxy. This would be sim-
ilar to the conduct of this liquid
with ethyl alcohol. This fact
caused the first series of experiments
to be made at ordinary pressure.
Exact experiments were then made
according to the method pursued
so successfully by Dashiell.

His method was to decompose
the mixture of the liquid ^{compound} with
alcohol, & evaporate the alcohol.

neutralize the resulting acids with barium carbonate and separate the hydrogen and ethoxy products by repeated extraction with 74 percent boiling alcohol. In this way by variation of first the total barium salts, then the weights of the part extracted by alcohol, and of the residue, it was possible to calculate the percentages of the products formed. The separation was based on the difference in solubility of the hydrogen and ethoxy salts in boiling alcohol the hydrogen product being but slightly soluble.

In the first series therefore three experiments were made under like conditions i. e. at ordinary pressure.

with absolute methyl alcohol. The
 indicator lamp, some of the liquid &
 compound were boiled while
 200° of absolute methyl alcohol in an
 Erlenmeyer flask connected with
 an inverted condenser. The decom-
 position of the ^{compound} began when
 the boiling of the alcohol commenced,
 also indicated by the change of color
 of the liquid and escape of gas. Color
 at first cherry red, at the end of the
 decomposition whitish brown.
 The reaction was complete in
 about one hour and fifteen min-
 utes. By this time all solid mat-
 ter had disappeared and the matter
 in alcohol simply boiled without
 the evolution of gas. Back stream
 was then connected with an ordinary

condenser and the product distilled from the product of the decomposition, as in the preliminary experiment the acid residue was converted into the barium salt by means of pure barium carbonate. The water solution of the barium salt was evaporated to dryness and dried in the air bath at 100° .

Experiment I	10 th	size	grav	13.54	}
"	II	"	"	13.49	
"	III	"	"	13.51	

Barium salt,

The three portions were again dissolved in water and evaporated to crystallisation, there first appeared a nearly white not well crystallised salt and then well crystallised yellowish

sometimes reddish brown tables
As was stated above these were
taken to be two different salts
if barium. Attempts to separate
them for analysis. The method
by alcohol as described by Du-
schell did not prove satisfactory
In order to get material for im-
mediate analysis the well crystal-
lised portion was separated me-
chanically from the white powder.
The tubular crystals were first
analysed. The determination
of the water of crystallisation
brought to light some inter-
esting facts. The salt begins
to lose water at 60° , at from
 110° to 150° the weight is constant
The loss in weight corresponding

closely to the loss of two molecules of water from the compound. On further heating to 165° the third and last molecule of water of crystallization was driven off and higher heating did not produce any further loss. The analysis for water of crystallization and barium gave the following results.

- I 0.2530 gram of salt lost at 165°
 0.0230 gram of water and gave
 0.0710 gram of barium sulphate
 II 0.2376 gram of salt lost at 165°
 0.0216 gram of water and gave
 0.0737 gram of barium sulphate.

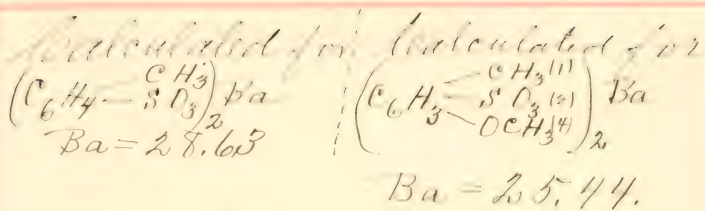
Calculated for $\left(\text{C}_6\text{H}_3 \begin{array}{c} \text{CH}_3 \\ \text{SO}_3 \\ \text{OCH}_3 \end{array} \right)_2 \text{Ba} \cdot 3\text{H}_2\text{O}$ Found

H_2O	7.11	7.09	7.05
Ba	23.13	23.02	23.10

Estimations of barium were now made with both the non-crystallised portion and also of the mixture of the well crystallised and non-crystallised which could not be separated mechanically. In the case of the white powder or non-crystallised portion it was not possible to determine water of crystallisation. The results did not agree with each other. The analyses were made from the white powder and the mixture after dehydrating at 165° and gave the following results.

- I. 0.2060 gram of the powder gave
 0.0792 gram of barium sulphate.
 II. 0.2377 gram of the mixture gave

0.1043 gram of barium sulphate.
 III 0.2086 gram of the mixture gave
 0.0896 gram of barium sulphate.
 IV. 0.2541 gram of the mixture gave
 0.1091 grams of barium sulphate.
 If the hydrogen reaction had
 taken place at all, one would
 expect to find the barium salt
 of ortho-toluene-sulphonic acid.
 The comparison of the percentages
 of barium in the above four analy-
 ses with the percentages of barium
 in barium ortho-toluene-sulphonate
 and in barium para-methoxy-ortho-
 toluene-sulphonate, would give
 a strong indication as to the course
 of the reaction. The calculated
 percentages are for the sulphonic
 salts.



Found

I	II	III	IV
25.47	25.58	25.26	25.26

In these analyses there is no evidence that the hydrogen reaction had taken place. If it had occurred at all it was in such small quantity as to escape detection by analysis. Further in collecting the gas given off during the decomposition no satisfactory evidence could be obtained of the presence of formaldehyde. The gas was nitrogen only. The different parts were

had been analysed for barium with the results stated above were changed into the sodium salt. This sodium salt treated with phosphorus pentachloride. The acid chloride thus formed was transferred into the amide by means of strong aqueous ammonia. There resulted only one amide melting at 150° . In fact all the derivatives and transformations subsequently made lend additional evidence that there was only one product formed. This product at ordinary pressure is para-methoxy-ortho-toluene sulphonic acid.

Experiment at increased pressure.
In order to study the influence
of pressure on the course of the re-
action one experiment was made
at an increased pressure of 2.00 mm.
and one experiment at a diminished
pressure.

The experiment at increased
pressure was conducted in the
apparatus used and described
by Palmer and others. This appa-
ratus consists of a strong one
and one-half liter balloon flask
covered with a close net-work
of copper wire (about one-quarter
inch mesh). This flask was fitted
with a two hole stopper (rubber)
which was bound down during
the experiment. Into one of the holes

was fitted a bent glass tube connected with an open end U-tube mercury manometer graduated in millimeters. Into the other hole through the stopper was fitted a copper tube, at the top of which was a conical valve provided with a lever on which was hung a leaden weight. By adjusting this weight any desired pressure could be obtained.

Ten grams of the diazo compound were decomposed with absolute methyl alcohol in the pressure flask at 200 mm pressure. The same phenomena were observed as at ordinary pressure only the decomposition lasted in about forty five minutes. The barium

Salt made from the acid produced, appeared like that formed from the product of decomposition at ordinary pressure. Analyses were made of the barium salt dehydrated at 165° , no attempt being made to separate any portions. The results are as follows.

I 0.1870 gram of substance gave
0.0809 gram of barium sulphate.

II 0.2153 gram of substance gave
0.0928 gram of barium sulphate.

Calculated for Found
 $\left(\text{C}_6\text{H}_3 \begin{array}{c} \text{CH}_3 \\ \text{SO}_3 \\ \text{OCH}_3 \end{array} \right)_2 \text{Ba}$ I II

Ba. = 25.44 25.44. 25.36.

The only product of the reaction is therefore the methyl sulphonic acid.

Experiment at diminished pressure.
 The experiment was also conducted at one half atmosphere pressure. The apparatus consisted of a strong one liter balloon flask fitted with a three hole rubber stopper. In one hole was a bent glass tube connected with a vacuum ^gage. Through the second ran a thermometer. The tube of an upright condenser passed through the third hole into the upper end of the condenser was fastened by means of a one hole rubber stopper the short arm of a twice bent glass tube, the long arm of which terminated a few millimeters below a two hole rubber stopper in a filtering flask. A test tube was placed

upright within the flask the open end being immediately below around the end of the long arm of the tube connected with the condenser. This tube served to collect the methyl alcohol should any distil over during the experiment. Through the second hole of the stopper in the filling flask passed a bent glass tube one end terminating in the bottom of the flask the other end connected with a Bunsen suction pump.

By this means if water should be drawn into the flask from the pump it would not interfere with the experiment and readmitting air into the apparatus the tube terminating in the bottom

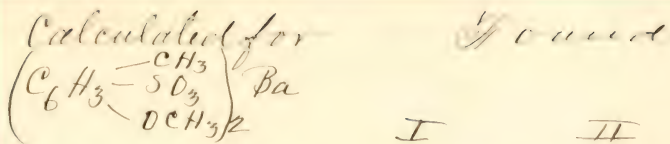
would conduct the water off completely, & a pressure inside of the apparatus was regulated by attaching a rubber tube to the side tube of the filtering flask and closing the rubber tube with a Mohr pinchcock. The pressure could then be regulated by hand by carefully watching the vacuum gauge or the thermometer the pressure could be kept constant for any length of time without varying more than 20^{mm} of pressure or 2° of temperature.

The diars compound and absolute methyl alcohol were introduced into the flask, the pump turned on and at one half atmosphere the flask was heated

in a water bath. The decomposition proceeded much slower than in previous experiments. The methyl alcohol boiled at 49° 51° pressure near 370^{mm} . 7.00 grams of diars^{compound} required six and one half hours for complete decomposition. The methyl alcohol was distilled from the product of decomposition, barium carbonate added, and the barium salt evaporated to dryness, dehydrated and analysed for barium with the following results.

I 0.1538 gram of substance gave
 0.0668 gram of barium sulphate.

II 0.1933 gram of substance gave
 0.0835 gram of barium sulphate.



Ba = 25.44 I II
25.55 25.41

As in the cases with ordinary and increased pressure only one product could be obtained and this was the methoxy compound.

Variation of the pressure does not change the course of the reaction.

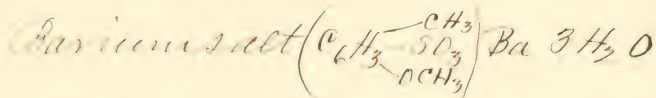
Para-methoxy-ortho-toluene-sulphonic acid.

In all subsequent experiments larger amounts of the diazo compounds were decomposed with methyl alcohol. One hundred grams of the diazo compound were decomposed with 500

liter of methyl alcohol, the product after distilling the methyl alcohol is a dark brown liquid easily soluble in alcohol and water. Made in large quantities it shows signs of crystallisation after standing twenty four hours. Set aside for several weeks it solidifies but not in well defined crystals. Boiling with animal charcoal does not entirely remove the color. After many attempts a small quantity of the acid was obtained in well defined rhombohedral plates of a yellowish brown color. It decomposes without melting. The acid purified as far as possible with animal charcoal or the acid derived from

the well crystallized barium salt was used for making salts.

Salts of para-methoxy-ortho-toluene sulphonic acid.

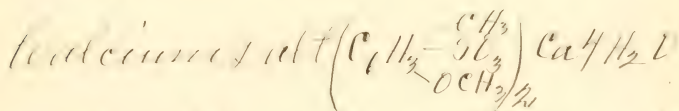


Analysis of this salt have already been given. This salt crystallizes from concentrated water solution in large monoclinic tabular crystals with three molecules of water.

Only the well crystallized is formed from the hot solution of thirty parts of the salt in one hundred parts of water. If the concentration is more than this the salt is first deposited from the hot solution in

the forming a white powder losing
 not than three molecules of water of
 crystallisation. Since the crystals
 begin to lose water at 60° also
 by standing in the air at ordinary
 temperature, it appears that
 even in boiling water at cer-
 tain concentration the salt loses
 some of its water of crystallisation
 probably two molecules.

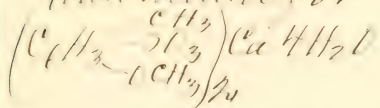
The salt is easily soluble in wa-
 ter, difficultly soluble in alcohol.



Prepared by neutralisation of the
 free acid with finely powdered
 calcite. Slightly soluble in water
 less so in alcohol. From water:

it forms a compact mass of lustrous transparent crystals.
 Analysis for calcium gave the following results.

- I. 0.2752 gram of the salt lost 17.0%
 0.0383 gram of water and gave
 0.0746 gram of calcium sulphate.
 II. 0.2402 gram of the substance lost
 16.335 gram of water and gave
 0.0677 gram of calcium sulphate.
 Calculated for $\frac{1}{2}$ molecule



		I	II
H_2O	14.01	13.40	13.44.
Ca	7.78	7.77	7.58

Magnesium salt $\left(\text{C}_6\text{H}_3 - \overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}} \right)_2 \cdot 6.5\text{H}_2\text{O}$

Prepared by neutralizing the

for acid with formic acid
carbonate, very soluble in water
and alcohol, from water the salt
crystallizes in radial tufts of
short slender prisms, from alcohol
in white plates.

Analysis for magnesium gave
the following results.

I 0.3172 gram of the salt lost 191°

0.0545 gram of water and gave

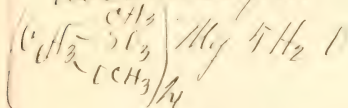
0.0767 gram of magnesium sulphate.

II 0.2174 gram of substance lost

0.0376 gram of water and gave

0.0495 gram of magnesium sulphate.

Calculated for $\text{C}_6\text{H}_5\text{MgCl}$



	I	II
H ₂ O	17.44.	17.07. 17.30.
Mg	4.65.	4.81. 4.55

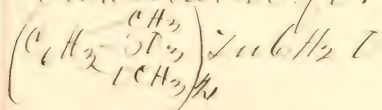
Zinc salt, $\left(\text{C}_6\text{H}_3 \begin{smallmatrix} \text{CH}_3 \\ \text{SO}_2 \\ \text{OCH}_3 \end{smallmatrix} \right)_2 \text{Zn} 6\text{H}_2\text{O}$

Prepared by neutralizing the acid with pure zinc carbonate easily soluble in alcohol and water crystallizes in short pointed prisms. Analysis for zinc gave the following results.

I 0.2491 gram of salt lost at 165°
 0.0461 gram of water and gave
 0.0344 gram of zinc oxide.

II 0.2791 gram of substance lost
 0.0541 gram of water and gave
 0.0387 gram of zinc oxide.

Calculated for $\text{C}_{12}\text{H}_6\text{O}_4\text{S}_2\text{Zn}$



		I	II
H_2O	11.77	11.71	11.75
Zn	11.34	11.09	11.14.

Sodium salt $C_6H_7- \overset{CH_3}{SO_3Na} \frac{1}{2} H_2O$.
 $-OCH_3$

Prepared by gradual precipitation of
 the methyl from the barium salt
 with a solution of sodium carbonate.
 Slightly soluble in water and alcohol.
 When suspended almost to dryness the
 solution on cooling solidifies into a
 compact mass of almost colorless
 leaflets. (Analysis given below.)

I. 0.2744 gram of salt lost at 161°
 0.0304 gram of water and gave
 0.0611 gram of sodium sulphate.

II. 0.2763 gram of substance lost
 0.0303 gram of water and gave
 0.0620 gram of sodium sulphate.

Calculated for $C_6H_7- \overset{CH_3}{SO_3Na}$
 $-OCH_3$

		<u>I</u>	<u>II</u>
H ₂ O	10.75	10.69	10.58
Ka	9.18	9.25	9.29

Potassium salt $C_6H_3 \begin{matrix} CH_3 \\ | \\ CO_2K \\ | \\ CH_3 \end{matrix} H_2O$

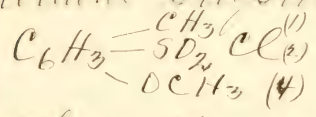
Prepared by exact precipitation of the material for the Methanum salt by a solution of potassium carbonate. Very soluble in water and alcohol. From the hot concentrated solution there is isolated a mass of almost colorless fine branching needles. Analysis gave the following results.

- I. 0.2247 gram of the salt lost 0.0160 gram of water and gave 0.0771 gram of potassium sulfate.
- II. 0.2319 gram of substance lost

0.0165 gram of water and 0.0777 gram of barium sulphate.
 Calculated for $C_6H_3SO_3K \cdot H_2O$
 $\begin{array}{c} C_6H_3 \\ | \\ -OCH_3 \end{array}$

		<u>I</u>	<u>II</u>
H_2O	6.77	6.97	7.1%
K	15.11	15.07	15.04.

Chloride of para-methoxy ortho
 toluene sulphonie acid.



The sodium salt made either
 by neutralising the free acid or
 with sodium carbonate or by
 precipitating the metal from
 the barium salt with a solution
 of sodium carbonate, was dried
 at 100°. The barium salt gave

stirred salt a slight excess began and
 of phosphorus pentachloride was added.
 The reaction soon began and
 proceeded with violence and
 evolution of considerable heat.
 Most of the phosphorus oxychloride
 was broken off by the heat of the
 reaction. The last portion of the
 oxychloride held back by the titanium
 chloride could not be entirely removed
 even when heated to 120° .
 On cooling the acid chloride was
 poured into a large amount of
 cold water and washed.

The chloride is a heavy oil yellow-
 ish white in color, very soluble in
 ether, from which it was not ob-
 tained crystalline but rather viscous
 and oil after evaporation of the ether.

Benzenesulfonyl chloride, $\text{C}_6\text{H}_5\text{SO}_2\text{NH}_2$.

Prepared by treatment of the acid chloride with strong aqueous ammonia. The reaction being complete, the aqueous ammonia was brought to boil vigorously, and after shaking for a short time the amide suddenly solidified into a greyish white mass. After evaporating off the excess of ammonia on the water bath and acidifying with hydrochloric acid, the amide was filtered, washed with cold water. The amide is very soluble in alcohol, in which it is best dissolved and decolorised with animal charcoal. It is then purified

from the hot concentrated alkaline solution as white plates. The amide is difficultly soluble in cold and hot water. From boiling water it crystallises in quadratic plates if rapidly cooled, if slowly in short prisms with a vitreous luster. Soluble in ammonia and in the alkaline carbonates from which it is precipitated on addition of acids. The amide melts at 151° . Mention has been made already that only one amide is formed from the product of the decomposition of the lignin with methyl alcohol. Working over the mother liquors failed to discover any trace of the amide of ortho-toluene sulphonic acid.

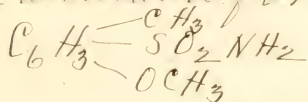
Analysis for sulphur and nitrogen gave the following results

I 0.3471 gram of the amide gave
0.4044 gram of barium sulphate.

II 0.3177 gram of the amide gave
0.3721 gram of barium sulphate.

III and IV determinations for
nitrogen after Kjeldahl.

Calculated for



Found

I

II

S. 15.94. 16.01. 16.09.

III

IV

N. 6.98. 6.79. 6.90

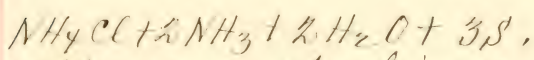
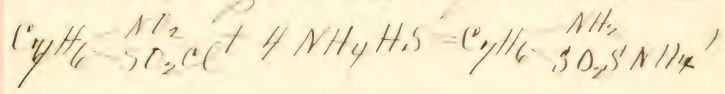
Comparison with the one which
 toluene sulfonic acid of Vignard
 and Heffter?

Heffter when studying benzoic
 acid toluene ether this sulfonic acid
 had changed this this sulfonic
 acid into the corresponding sul-
 fonic acid, but in polymerizing the
 para-amino-ortho toluene sulfonic
 acid and decomposing heating
 o-coupled in absolute methylal-
 coh. he obtained a more volatile
 sulfuric acid which he called $C_{12}H_{10}O_4$
 methyl toluene sulfonic acid and
 gave the formula $C_{12}H_{10}O_4 - \frac{C_{12}H_{10}O_4}{C_{12}H_{10}O_4}$

This acid is apparently identical
 with the product obtained in this
 investigation when present

ortho-toluenesulphonic acid was
 decomposed with strongly alcohol.
 As Hoffers description of Heuss's
 ortho-toluenesulphonic acid was not
 in all particulars
 with the description of compounds
 of the ortho-toluenesulphonic acid
 already given in this thesis
 it was thought advisable to re-
 peat his experiments, for the pur-
 pose of comparison. The short-
 ing point of Hoffers experi-
 ment was that ortho-toluenesulphonic acid, the che-
 mical of Heuss's acid made by heat-
 ing the ortho-toluenesulphonic acid with
 phosphorus pentachloride acid
 crystallized from ether, when
 treated with alcohol, gave a

sublimed, however, with the
ammonium salt of benzoic acid
or the benzoic acid sulfonic acid,
according to the equation



After concentration of the liquid
and removal of the separated
sulfur, the difficultly soluble
free benzoic sulfonic acid is pre-
cipitated by acetic acid.

This reaction was performed
and the acid obtained as describ-
ed in hard yellowish crystals.
The change to the sulfonic acid
is effected by boiling with hy-
drochloric acid or by means
of sodium amalgam.

advises the latter. Therefore if
 60 g. of the sodium salt
 of the trisulphonic acid were
 reduced by about 600 g. of sod-
 ium amalgam made by bring-
 ing together 60% of mercury
 and 40 grams of metallic sodium.
 By this reduction the nature
 of the H₂S group is changed
 to hydrogen sulphide. Addition
 of acetic acid precipitated the
 sulphonic acid $C_6H_3(SO_3H)_3$.
 $N \cdot H_2$ (?)

Crystallized from hot water the
 acid was obtained in colorless
 hard prisms.

The triazene compound of the
 sulphonic acid was made by
 Hefter by passing nitrous acid

intercolleated absolute alcohol
 in which the finely divided sublimic
 acid was suspended. The
 dihydro compound forms yellow
 to brown matter which on some
 colored like mastic. It is not
 soluble in alcohol. It decomposes at ordinary
 temperatures with separation of
 a brown resin insoluble in al-
 cohol and ether. The dihydro com-
 pound in alcohol decomposes
 considerably even at ordinary
 temperature and completely by
 warming under ordinary pres-
 sure. No aldehyde was given off.
 To the clear alcoholic solution
 water was added and after fil-
 tering from the precipitated
 resin, evaporated and the re-

by residue changed into the
barium salt of para-ethoxythio-
toluene sulfonic acid. $C_{11}H_7SO_3$ $\begin{matrix} 5H_2 \\ 5O_3 \\ 1C_2H_5 \end{matrix}$

Knoblich and Hoffer mention
the work of Jussieu on the ring of
para-ethoxythio-toluene sulfonic
acid. This ring of Jussieu
could not decompose with
ethyl alcohol except under a
pressure of 300 mm. when other
thio-toluene sulfonic acid was present.
The difference in behavior of the
two rings compounds with
alcohol and water caused
Knoblich and Hoffer to make the
statement that the two rings or
compounds were not identical
although they obtained a para-

From ortho-toluene sulphonic acid identical with that of Hansma. Since Hansma and Palmer in 1886 obtained the ethoxy product by decomposing the ether of para-amido-ortho-toluene sulphonic acid at increased pressure the question naturally arises whether the para-ethoxy-ortho-toluene sulphonic acid obtained by them was identical with that of Vignoblet and Heffler. The answer must be given not the same, because the acids melt differently. Vignoblet and Heffler give the melting point at 136° , Palmer 143° & 144° U.S. Hansma's has been obtained in considerable quantity and in a very pure condition by Palmer.

Palmer Chem Jour 6-2345

and afterwards by Sanfield and
 both give the melting point at
 143° 144° which is undoubtedly
 correct.

There were also differences noticed
 in the descriptions given by
 Sanfield and Hauffler for para
 methoxy or the toluene sulphonic
 acid, its barium potassium
 salts and the descriptions given
 in this thesis. They describe the
 acid as non crystallising giving
 a barium salt which decomposes
 by evaporation of its water solu-
 tion attended with the strong od-
 or of cresol, and without con-
 stant decomposition. The toluene
 a viscous yellowish oil, melting
 melting at 15° .

In this work the acid was obtained in well defined crystals the barium salt well crystallized and of constant composition and without color if dissolved in boiling the water solution of the salt.

The description of the chloroamide amide agree closely.

In making the pure methyl ester toluene sulphonic acid according to the method of Gumprecht and Heffler the reactions and products were found to correspond with their description. The diars^{compounds} of the sulphuric acid was suspended in absolute methyl alcohol, with alcohol and nitrous fumes passed through.

The diars^{compounds} appeared in a short time as brown needles, there were quantities

filtered and washed a few times
with methyl alcohol. The residue
was then placed in a flask with
methyl alcohol, reaction pro-
ceeded at ordinary temperature
and by warming in the water bath
|| was over in a short time. Water
was added, the precipitated mass
filtered off, and the filtrate evap-
orated in the water bath. Barium
carbonate was then added, the
barium salt filtered from the
excess of barium carbonate
and evaporated to dryness, absor-
bing the residual salt was dis-
solved in absolute alcohol by
boiling. After cooling addition
of ether precipitated the salt as
a yellowish powder as described

ed by Haffner, so far the work
of Haffner was repeated.

Efforts were now made to obtain
the salt in crystallised form, by crys-
tallising from water. The experience
obtained by working with large
quantities of the barium salt of the
methoxy acid, had indicated the best
method to pursue. Now if it were
possible to obtain from water
solution crystals of the barium
salt obtained by the method of
Grimm and Haffner, like the
crystals of the barium salt of the
methoxy toluene sulphonic acid
obtained by the decomposition
of the diars of para-amide with
toluene sulphonic acid in methyl
alcohol strong evidence would

~~resulted~~ the furnishing of the iden-
 tity of the two products. The di-
 id barium salt, and the portion precipi-
 tated by silver from the alcoholic sol-
 ution were dissolved in water and
 boiled with animal charcoal.
 After filtering, the solution of the
 salt was light yellow ^{and was} exposed
 to crystallization. On cooling of the
 concentrated solution there first ap-
 peared a white powder then well
 defined crystals like the barium
 salt, described at the beginning
 of this series. The yield of barium
 salt was very small, twelve grains
 of the sulphuric acid giving but
 little more than a grain of the
 barium salt of the malonic acid.
 Heffner says that eight grains

of the sulphuric acid more cubic
 mass of the pure barium salt of
 the chloroacid while the yield of
 the methoxy salt was still smaller.

400 analyses were made and
 gave the following results.

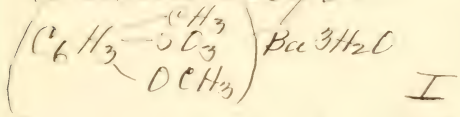
I 0.2588 gram of the salt lost.

0.0232 gram of water and gave

0.1036 gram of barium sulphate.

II 0.2739 gram of salt & after when
 dehydrated at 165° 0.1202 gram
 of barium sulphate.

Calculated for Found



H₂O 9.11. 8.96

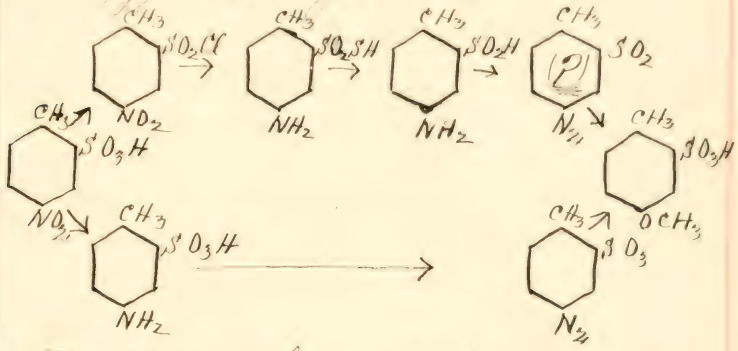
Ba 23.13. 23.55

Calculated for dehydrated salt

Ba 25.44. 25.77 25.89

The differences are now narrowed down to the crystallising power of the acid. But it must be said that only when working with large quantities of the acid is it possible to detect any signs of crystallisation. As Sigmund and Ruffler worked only with very small quantity of the acid it is not surprising that it was not obtained crystalline. The conclusion seems to be justified that the two nitroxy acids are identical. Whether the base compounds from which the acids are derived are identical or not is a question to which answer is not attempted at this time. A comparison of the two methods starting from nitro toluene sulphonic acid and meeting again in the

methoxy acids is given below,



To obtain the methoxy acids
 very short study of the transformations
 by the two methods would
 soon convince one which is the
 better one to follow. The method
 described in this paper gives
 large and very satisfactory yields
 at every stage from the nitro-
 toluene to the methoxy acid.

Reaction of Potassium and Sulphuric
on para-methoxy, ortho-toluene
sulphonamide.

Remond and Guldberg¹ by oxidising
ortho-toluene-sulphonamide with
potassium permanganate obtained
the first member of a class of bodies
to which has been ascribed the
name of "sulphinide". Since this
discovery, other members of this
class have become known. The
directions given in the first arti-
cle for the preparation of benzo-
ic sulphinide or "saccharine" were
followed. 10 grams of para-meth-
oxy-ortho-toluene-sulphonamide
45 grams of potassium permangan-
ate with 20 c.c. of water were
placed in a one-litre flask

1/2 strength, vol. 1-426

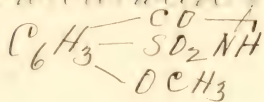
liler flask sunk in water and heated for some hours at the boiling temperature of water. The color of the permanganate disappeared in about three hours. The solution was then filtered from the insoluble manganese compounds and evaporated to a small volume. Addition of hydrochloric acid produced a white precipitate of fine needles. After filtering and washing the precipitate in cold water it was dissolved in boiling alcohol. The compound is easily soluble in hot alcohol, difficultly in cold. Any unreacted chromide is thus easily separated as it is quite soluble in cold alcohol. From alcohol the melting point

zinc sulphinate crystallises in beautiful long blade like crystals. It is difficultly soluble in boiling water. On cooling long slender needles four to six centimeters in length appear. The crystals melt at 271° .

Analysis for sulphur and nitrogen show this compound to be paramethoxy benzoic sulphinate. The following ^{are the} results of analysis

- I. 0.1654 gram of the substance gave 0.1706 gram of barium sulphate
- II 0.1733 gram of substance gave 0.2025 gram of barium sulphate
- III and IV Determinations for nitrogen after Kjeldahl (Gunning modification)

Calculated for



Found

S 15.04

15.00 — 15.18

N 6.59

6.47 — 6.74

Barium salt of methoxy benzoyric sulphimide ($\text{C}_6\text{H}_3 - \text{SO}_2\text{NH} - \text{OCH}_3$) in $3\text{H}_2\text{O}$

Two grams of methoxy benzoyric sulphimide were dissolved in boiling water and pure barium carbonate added. After boiling sometime the excess of barium carbonate was filtered off and the filtrate evaporated to a small volume. The salt is easily soluble in water from which it

crystallises in large colorless needles concentrically arranged.

The anhydrous salt was washed with absolute alcohol, recrystallised from water and analysed for water of crystallisation and barium with the following results.

I 0.2438 gram of the salt lost

0.0215 gram of water and gave

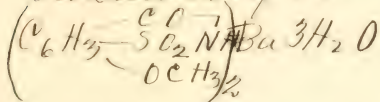
0.0920 gram of barium sulphate.

II 0.1160 gram of substance lost

0.0166 gram of water and gave

0.0701 gram of barium sulphate.

Calculated for Found



I.

II.

H₂O 8.78. 8.82. 8.92.

Ba 22.29. 22.19. 22.17

Acid potassium salt of
para-methoxy ortho-sulpho-
benzoic acid. $C_6H_3 \begin{matrix} \text{COOH} \\ \text{SO}_3K \\ \text{OCH}_3 \end{matrix} H_2O$

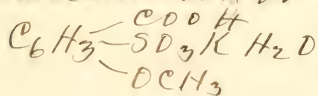
If the filtrate from methoxy-
benzoic sulphinate be evapora-
ted almost to dryness potassium
chloride first crystallises then
long beautiful prisms almost
colorless, which proved to be
the acid potassium salt of para-
methoxy ortho-sulphobenzoic acid.
This salt can be obtained from
these mother liquors either by
fractional crystallisation to free
it from potassium chloride or
evaporating to dryness and ex-
tracting with alcohol. The salt is
much more soluble in alcohol

than potassium chloride, and may thus be obtained pure. Analysis of the salt gave the following results.

I 0.668 gram of the salt lost 0.0166 gram of water and gave 0.0771 gram of potassium sulphate.

II 0.2224 gram of substance dehydrated at 125° gave 0.0714 gram of potassium sulphate.

Calculated for $\text{C}_6\text{H}_3\text{SO}_3\text{K} \cdot \text{H}_2\text{O}$ Found



H_2O 6.25 6.32

K 13.58 13.43

Calculated for dehydrated salt.

Found

K = 14.44

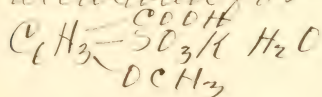
14.41

The acid potassium salt was made also by oxidising the potassium salt of para-methoxy-ortho-toluene-sulphonic acid. 10 grams of this salt were dissolved in one liter of water, 15 grams of potassium permanganate added and heated in boiling water. The color of the permanganate disappeared in about two hours. After removing the insoluble manganese compounds and evaporating to a small volume, strong hydrochloric acid throws down the acid potassium methoxy-sulphobenzoylate as short needles. These needles recrystallized from water and analysed gave the following results.

Found 766 grams of the salt lost.

0.0174 gram of water substance
 0.0842 gram of potassium sulphate
 II 0.2763 gram of the dehydrated
 salt gave 0.0894 gram of pot-
 assium sulphate.

Calculated for Found



H₂O 6.25

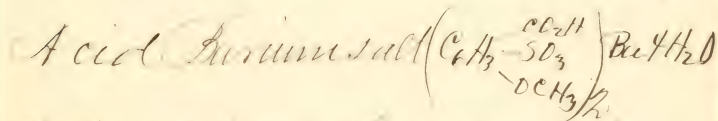
K 13.58

Dehydrated K 14.44

I 6.29

13.66

14.99



Prepared from the free monobasic
 sulphotriazolic acid. A water solu-
 tion of the acid was divided into
 two equal parts, one part neu-
 tralised with barium carbonate

1/5 This neutral barium salt the second part of the acid was added to produce the acid salt. Both the neutral and acid salts are extremely soluble in water and were not obtained in crystals. I a by double-^{acid} the acid barium salt is difficultly soluble, from which it crystallizes in fine white needles, analysis gave the following result,

0.2212 gram of the substance lost 0.0234 gram of water at 180° and gave 0.0761 gram of barium sulphate.

Calculated for		Found	
$\left(\begin{array}{c} \text{C}_6\text{H}_3 \\ \text{SO}_3 \\ \text{CH}_3 \end{array} \right)_2 \text{Ba} \cdot 4\text{H}_2\text{O}$		I	
H ₂ O	10.72		10.58
Ba	20.44		20.24

Benzic sulphuric acid $\text{C}_6\text{H}_5\text{SO}_3\text{H}$ (1)
 $\text{C}_6\text{H}_5\text{SO}_3\text{H}$ (2)
 $\text{C}_6\text{H}_5\text{SO}_3\text{H}$ (3)

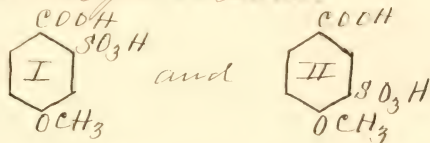
This acid was first prepared from the acid potassium salt by converting the salt into the chloride by means of phosphorus pentachloride, then decomposing the acid chloride in boiling water, evaporating, & drying and recrystallizing from water. A second method is to pass from the methoxy benzoic sulphuric acid to the acid. This is accomplished by boiling the methoxy benzoic sulphuric acid in dilute hydrochloric acid, one part of the concentrated acid to eight parts of water & in the case of benzoic sulphuric acid ammonium salt of the same

responding acid is formed.
 This acid ammonium salt when
 treated with twice its weight of
 phosphorus pentachloride gives the
 chloride. When this chloride is boil-
 ed with water sulphochloric acid
 is given off and the acid is formed.
 Crystallized from water in which
 it is quite soluble this acid appears
 as long interlacing needles, trans-
 parent and colorless. It melts
 without decomposition at 104° .
 on cooling it quickly solidifies
 and again melts at the
 same point. This may be repeated
 without change of the melting
 point.

chloride of para-methoxybenzyl
sulphobenzoyl acid $C_6H_3SO_2Cl$
 $\begin{array}{c} \text{COOCl} \\ \text{OC}_6H_3 \end{array}$

The chloride prepared as above
described for the preparation
of the methoxy sulphobenzoyl acid
is a white solid, it does not
solve easily in ether from which
it crystallises in small hard
crystals transparent and colorless.
The crystals powdered and boiled
with aqueous ammonia give the meth-
oxybenzoyl sulphinic acid, melting at
87°.

Comparison of Laro's method
 with sulphobenzonic acid with
 the sulphamic acid of Laro as
 benzoic acid C_6H_5COOH (I) according
 to theory should give two sulphonic
 acids, one in which the sulphonic
 acid group would be in the ortho
 position to carbonyl the other
 in the meta position.



By derivation the acid described
 in this paper should be the one
 expressed by formula I

It was thought advisable to re-
 peat the experiments of Laro as
 follows; 5 grams of crystalline
 benzoic acid in a small balance



flask were covered with fuming
 sulphuric acid and heated in a
 water bath for two hours. After
 cooling the contents of the flask
 were poured into cold water.
 This solution of sulphamic acid
 and the excess of sulphuric acid
 was neutralised with pure lead
 carbonate. The lead sulphate
 was filtered off and repeatedly
 washed with hot water. The lead
 salt as described by Dewar was
 found to crystallise from hot
 water in beautiful transparent
 crystals. The lead salt was trans-
 formed into the sodium salt by
 precipitation of the water with
 a solution of sodium carbonate.
 A portion of this salt was found

in a silver crucible with potassium
 hydroxide. The fused mass was
 dissolved in water and acidified
 with hydrochloric acid. Sulfur
 dioxide was given off. The solu-
 tion was extracted with ether.
 After evaporating the ether there
 appeared needles of protocatechuic
 acid. A portion of the crystals
 was dissolved in water and this
 solution gave the characteristic
 color reaction with ferric chloride
 namely dark green. Addition of a
 very little sodium carbonate
 changed the green color blue
 passing rapidly into red. The
 melting point of the needles from
 ether was found to be 194° .
 The melting point of protocatechuic

acid is variously given by different observers. Malin¹ who first made this experiment with sulphamic acid, gave 177° as the melting point. Barth and Schmitt² gave the melting point of pure protocatechuic acid as 174° (uncorr). The melting point here found as is apparently agrees with that given by Barth and Schmitt.

In the same manner two grams of methyl benzoic sulphinate were fused with ten grams of potassium hydroxide, the fused mass dissolved in water acidified and extracted with ether. The crystals obtained after evaporation of the ether, dissolved in water gave

a purple coloration with ferric chloride. The temperature of the fusion with potassium hydroxide was not determined and as Gabbler² in fusing 1, 2, 4, disulphobenzoylic acid with potassium hydroxide had observed that at temperatures above 250° only resorcin is formed, below 250° 1, 2, 4, dioxybenzoic acid together usually with a small quantity of resorcin. It was thought that the purple color resulted from the blue color given by resorcin and the dark-red color of 1, 2, 4, dioxybenzoic acid. This conclusion proved correct. To the solution giving the purple coloration sodium carbonate was added, ethanol

1/ Amer Chem Jour 25-195

extracted only resorcin, which gave the characteristic blue coloration with ferric chloride and melted at 104° - 107° .

The solution from which the resorcin had been removed was acidified and extracted with ether. After evaporation of the ether, fine white needles were left behind. A solution of the crystals gave a dark red coloration with ferric chloride characteristic of 1,3,4, dioxy benzoic acid.

This acid is also described in chemical literature as β resorcylic acid. The only known ^{acid} salt from ether melted at 512° to 513° . This melting point agrees with that ascribed to β resorcylic

acid by Distrycki and Kost-
micki. These writers in their ac-
count of the formation of 3-resorcy-
lic acid from resorcin by heating
with potassium bicarbonate state
that on heating rapidly the white-
brown acid melts at 213° . This
statement is confirmed. Other
writers give a different figure
Blomstrand 194° Hultberg 194°
Benedikt and Hazura 194°
Fischer and Brunner 194° - 200°
Trennam and Perrissius 204° - 206°
The products of the fusion of
methoxy benzoic sulphonic acid with
potassium hydroxide therefore
are resorcin and 3-resorcylic acid
while sulphamic acid gives
protocatechuic acid and sulphur

be expressed by formula II (p. 73)
 The descriptive name of sulphuric
 acid would be penta-methoxy,
 meta sulphobenzoyric acid.

Summary.

I. When para-toluenesulphonic acid is decomposed with absolute methyl alcohol at ordinary, increased, or diminished pressure only the methoxy product is formed namely para-methoxy, ortho-toluenesulphonic acid.

II This result does not conform to the rules deduced from the study of the decomposition of diaryl compounds with ethyl alcohol but does confirm the suggestion that the simpler alcoholic group is introduced more easily than the more complex ones.

III The product of the reaction is identical with the ortho-methyl tol-
uenesulphonic acid obtained by

Diethylacetal after its hydro-
composition of the ring a compound
from para-amido ortho-toluene
sulphonic acid with methyl alcohol.

IV When para-methoxy ortho-toluene
sulphonic-acid is oxidized with
potassium permanganate para-
methoxy ~~sulpho~~ benzoic sulphonic
is formed. From this can be ob-
tained para-methoxy ortho-sulpho
benzoic acid.

V. Para-methoxy ortho-sulpho be-
zoic acid is isomeric with sulphi-
nic acid and by fusion with
potassium hydroxide, resorcin
and β -norsalicylic acid are formed.

Note.

I The temperatures given in this dissertation are all uncorrected.

II The atomic weights used in the calculations of this work are as follows.

Ba	136.9	S	31.92
Ca	39.91	O	15.96
Mg	23.94	H	1.
Zn	65.1	N	14.01
Na	23.	C	11.97
K	39.03		

Biographical Sketch.

The author of this dissertation, Robert
 Milton Parks, Jr. was born at South
 Indiana July 25, 1851. He prepared
 for college in the High School of Frank
 lin Ind. In 1875 he entered Indiana
 University and graduated in 1879
 with the degree of Bachelor of Arts.

Six years were spent in teaching four
 of which as instructor in the natural
 sciences in college and institutions.

Advanced courses of study were pursued
 by him at Harvard University 1882 and
 the University of Munich Germany 1883.

Three years as a graduate student at
 the Johns Hopkins University with his in-
 vention as the principal subject in zoology
 and geology the two subdivisions.





